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THE INTERACTION OF MOLECULES IN A SORPTION FILM UNDER HIGH PRESSURE

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In prior work by the author it has been shown that the adsorption isotherm of methane on activated carbon first rises with increasing pressure. In the pressure range of 50-100 kilograms per square centimeter a maximum is reached and the sorption drops thereafter, reaching a value of zero at 700-900 kilograms per square centimeter. This is in accordance with Gibbs' equation

$$\chi = X - \Delta \sim \delta_2$$

which defines sorption as a difference between the maximum amount of sorption X and the increase in volume of the sorbent (this increase includes the volume of the adsorbed substance) times the density of the gas phase δ_2.

At high pressures the density of the gas which is being adsorbed rises and the right-hand term increases faster than X -- consequently the isotherm must pass through a maximum. The behavior of fossil coal is different from that of activated carbon. As distinguished from that for activated carbon, the isotherm does not show a maximum: sorption first rises and then becomes constant at about 100-150 kilograms per square centimeter. Obviously, the adsorbed methane here does not occupy a new space which is distinct from the original volume of the coal and the volume of coal does not increase in the process of sorption.

The explanation lies in the water content of the coal, which has not been removed by the simple drying in vacuum at a maximum temperature of 35-40 degrees which preceded the author's experiment and cannot be eliminated even by much more drastic means, in view of the fact that the water is adsorbed by the coal. This water enters into combination with methane, forming the hydrate $CH_4 \cdot 6H_2O$. The adsorbed molecules of water are oriented and the water has a crystal structure corresponding to ice. This structure is loose enough to permit

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penetration of the methane molecules between the atoms: no over-all increase of volume takes place during the adsorption.

The second term of Gibbs' equation equals zero and the sorption remains constant. Saturation with methane hydrate over the whole surface occurs at a water content of approximately 8 percent in the case of most fossil coals. If the water content is insufficient, normal adsorption on the carbon surface takes place to some extent and highs develop on the isotherms as a result of the addition of two effects.

Some of the data used by the author was obtained with natural gas, i.e., impure methane, but this did not affect the results.

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